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(54) PROCESS FOR MANUFACTURING GELS CONTAINING IRON AND MOLYBDENUM AND THE USES THEREOF

- (71) We, INSTITUT FRANCAIS DU PETROLE DES CARBURANTS ET LUBRIFIANTS, a French Body Corporate, of 1 & 4 Avenue de Bois-Preau, 92 Rueil-Malmaison, Hauts de Seine, France, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- This invention concerns the preparation of transparent gels containing iron and molybdenum, and the uses of these gels, particularly as light filters or as precursors of mixed oxides containing iron and molybdenum oxides, some of which may be used as catalysts in the oxidation of primary alcohols to aldehydes, and more particularly of methanol to formaldehyde.
- According to the invention there is provided a process for manufacturing a transparent gel containing molybdenum and iron, comprising mixing at least one molybdenum compound as hereinafter defined with at least one ferric compound and, optionally, with at least one compound containing, in simple cationic form, a metal M selected from cobalt, nickel, manganese, chromium, scandium, yttrium, and the rare earth metals of atomic numbers from 57 to 71 inclusive, in the presence of a quantity of water not greater than that required to form individual saturated aqueous solutions of the compounds, and at a temperature between the freezing temperature of the saturated solutions of the compounds and 150°C, the compounds being used in such amounts that the atomic ratio $M/(Fe+M)$ is from 0 to 0.5 and the atomic ratio $Mo/(Fe+M)$ is from 0.4 to 5.
- In this specification the term "molybdenum compound" represents a fresh molybdic anhydride or any salt comprising a molybdenum-containing anion, except the alkali metal molybdates, the use of which would result, in the best cases, in opaque and heterogeneous gels.
- Our copending Application No. 63306/69 (Serial No. 1,282,949) also concerns a process for manufacturing a transparent gel containing molybdenum and iron. However, the relative proportion of solvent used in that process is greater than that used in the process of the present invention.
- Gels obtained by the process of the invention contain complexes of ferric ions with molybdenum ions.
- The reactants may be mixed with one another in any known manner. The mixture of the reactants which is initially in the form of a powder or a paste, is transformed either to a homogeneous paste or a clear solution. Each of these spontaneously hardens to a transparent, crystallographically amorphous, hard and brittle gel.
- When only molybdenum and ferric compounds are used the ratio of the number of molybdenum atoms to the number of iron atoms (Mo/Fe) in the reactants is from 0.4 to 5 and the atomic ratio (Mo/Fe) in the resulting gel is also from 0.4 to 5.
- According to a modification of the process of the invention, the molybdenum compound is also mixed with at least one compound containing, in the form of an oxygen-containing complex, a metal N selected from tungsten, chromium, manganese, uranium and vanadium. In this case the compounds are used in such amounts that the atomic ratio $(Mo+N)/(Fe+M)$ is from 0.4 to 5, and each of the atomic ratios $N/(Mo+N)$ and $M/(Fe+M)$ is from 0 to 0.5.
- The ammonium salts are preferred (for example ammonium molybdate, heptamolybdate or dodecamolybdate). Optionally, a small amount of ammonia may be added to the molybdenum compound.
- When a compound containing tungsten,

chromium or manganese, in the form of an oxygen-containing complex is used, this compound is preferably an ammonium salt. However, when uranium or vanadium is used, it is preferably in the form of an oxygen-containing complex such as a uranyl or vanadyl complex e.g. uranyl nitrate or vanadyl oxalate since the ammonium uranates and vanadates can hardly be used. When a vanadyl salt is used, an oxidizing substance such as hydrogen peroxide should be added to the starting mixture of compounds. Those metals that may be used in the form of simple cations (iron, cobalt, nickel, manganese, chromium, scandium, yttrium and the rare earth metals) are preferably introduced in the form of salts, for example, nitrates, chlorides, acetates, formates, carbonates, bromides, oxalates or sulphates. The nitrates and sometimes the chlorides are preferred. These salts may be used together with small amounts of inorganic acids, for example, nitric acid, sulphuric acid or perchloric acid.

The ferrous salts should be avoided since their reducing power is such that, when they are mixed with ammonium molybdates, molybdenum blues are produced whose separation makes difficult conversion of the resulting mixture to a gel. The starting compounds are generally used in their normal hydrated forms (for example 4 molecules of water per molecule of ammonium paramolybdate or 9 molecules of water per molecule of ferric nitrate). However, they can alternatively be used in a partially dehydrated form, particularly when the metal is Fe or a metal M.

Water may, if necessary, be added to a mixture of the compounds. However, the total amount of water used must not exceed that required to form individual saturated aqueous solutions of the starting compounds. The maximum amount of water that can be used depends on the temperature at which the mixture is made: for example, when $\frac{1}{2}$ mole of ammonium paramolybdate tetrahydrate and 2 moles of ferric nitrate nonahydrate are mixed at 20°C, the amount of water present must be less than 800 ml.

In most cases, the process of the invention directly provides, i.e. without dehydration, gels having a low content, for example from 10 to 30% by weight, of water. However, the gels may, if desired, be dried at a temperature of from 40 to 150°C.

A part of the water may be substituted by any polar organic or inorganic solvent, for example, a primary, secondary or tertiary alcohol, either aliphatic or aromatic, a diol, polyol, amine, amino-alcohol, amide, aldehyde, ketone, acid, acid-alcohol, keto-acid or amino-acid, tetrahydrofuran, dioxan or formamide or a derivative thereof, fur-aldehyde or dimethylsulphoxide, i.e. any sol-

vent favouring the reaction between the starting compounds. Where a solvent other than water is used the amount of water plus solvent must not exceed that required to form individual saturated solutions of the starting compounds.

A soluble inorganic salt, such as ammonium nitrate, ammonium chlorate or ammonium perchlorate may be added to the starting compounds or reactants. The solid reactants may be mixed by mechanical crushing. This is generally carried out by first roughly crushing the solid reactants, for example in a mortar, and then introducing the crushed reactants into a crushing apparatus such as a mixer, a roll-mixer or a mortar mixer. A mixer with sigmoid blades gives the best results.

The mixing should be carried out for a time sufficient to obtain a gel. When the reactants are crushed together, either of two types of reaction may take place, according to the atomic ratio $(\text{Mo}+\text{N})/(\text{Fe}+\text{M})$ in the mixture of the starting materials.

When the atomic ratio $(\text{Mo}+\text{N})/(\text{Fe}+\text{M})$ is from 0.4 to 1.5, the powder resulting from the mixing of the solid reactants transforms in a few minutes to a clear solution having a viscosity lower than 1000 centipoises at 20°C. When this solution is heated to a temperature which is preferably from room temperature to 150°C, while the mechanical crushing is continued, it becomes viscous and finally results in a homogeneous, rubbery and transparent gel.

When the atomic ratio $(\text{Mo}+\text{N})/(\text{Fe}+\text{M})$ is higher than 1.5, the powder resulting from the mixing of the solid starting materials is transformed in a few minutes into a solution having a viscosity higher than 1000 centipoises at 20°C; this solution, which contains a few undissolved crystals, gives a homogeneous, rubbery and transparent gel.

The time necessary to transform the solution to a gel in the two above reactions is dependent on the type of mechanical crushing and the temperature at which this crushing is carried out. For example, when a mixer having sigmoid blades is used and the atomic ratio Mo/Fe is 1, the time required for the solution to change to a gel at 70°C is 3 hours. When the atomic ratio Mo/Fe is 2, the time required at 20°C is 30 minutes.

The transparent gels obtained according to the process of the invention as described above may be used as light filters. They may be shaped by pilling, extruding, crushing or pouring and fragmenting before they are dried or heated. When these gels are subjected to a further crushing for at least 2 hours at a temperature of from 20 to 150°C, a powdered substance, that has a pale yellow colour when only iron and

molybdenum compounds are used, and other colours when other metal compounds are used, is produced. Water escapes more easily, and therefore the resulting powdered substance contains less water, if air is passed through the treated mixture. This powdered substance has a water content of lower than 10% by weight. It is amorphous from the crystallographic point of view and may be easily shaped by pilling, extruding or granulating. This shaping is of major interest when the powdered substance is to be used as a precursor of a catalyst for oxidizing primary alcohols to aldehydes and more particularly methanol to formaldehyde, said use being described hereinafter.

The gels and powdered products may be converted to mixed oxides containing iron and molybdenum and, optionally, other metals M and/or N, by heat decomposition at a temperature of from 300 to 500°C, preferably 350 to 470°C, generally for a time shorter than 6 hours, for example from 1 to 5 hours. This heat decomposition may follow a dehydration, for instance in an oven, at a temperature of from 40 to 150°C, preferably from 50 to 90°C, generally for at least 6 hours and preferably for from 24 to 72 hours. The thus-treated gels slowly dehydrate to form other gels which are also amorphous from the crystallographic point of view and transparent in the visible and infra-red range.

Some of these mixed oxides may be used as catalysts for oxidizing primary alcohols to aldehydes and particularly methanol to formaldehyde. The mixed oxides that may be used as catalysts are those resulting from the heat decomposition of those gels and powdered substances in which the atomic ratio $(\text{Mo} + \text{N})/(\text{Fe} + \text{M})$ is from 1.5 to 5. The molybdenum and iron compounds used to prepare the catalysts are preferably ammonium molybdate and ferric nitrate.

The temperature of the gel or powdered substance, during the heat decomposition, must not exceed 500°C, since overheating may result in a de-activation of the resulting catalyst.

The catalyst is a green to yellowish green solid when only iron and molybdenum compounds are used; its colour may change according to the nature and the content of additives. It has a fair mechanical strength; its specific surface area is from 0.5 to 20 m² per gram and the best results are obtained with catalysts having specific surface areas of from 4 to 12 m² per gram. The catalyst may be diluted by means of a catalytically inert material having a convenient grain size. The ratio by volume of catalyst/ (diluent + catalyst), may range from 0.1 to 1. The grain size of the diluent is preferably as close as possible to that of the catalyst.

The catalytically inert material may have

various different shapes (for example it may be in the form of balls, cylinders or rings). It may consist, for example, of a ceramics material, alumina, silica, silico-alumina, glass or silicon carbide.

The particles of the diluent may be either mixed with the particles of the catalyst or used in the form of one or more beds over, below or inside a bed of the catalyst; generally they are used before, behind or inside a bed of the catalyst.

According to their place of use, the diluents may improve heat exchange in the catalyst bed. They may also reduce the abrading phenomena in the catalyst bed and limit the pressure drop therethrough.

The oxidation of methanol to formaldehyde is carried out by passing a mixture of vaporized methanol and a molecular oxygen-containing gas through a bed of the catalyst at any pressure preferably close to the atmospheric pressure; the catalyst bed is preheated to a temperature of from 250 to 450°C, preferably of from 300 to 400°C.

The molecular oxygen-containing gas may consist of oxygen diluted with nitrogen or any other gas that is inert with respect to the reaction, e.g. steam or carbon dioxide. The proportions of inert gas and oxygen may be selected at will, provided explosion hazards are avoided. Air may be used instead of the mixture of nitrogen with oxygen, in which case the proportions of air and methanol used are usually from 3 to 15% and preferably from 5 to 7% by volume of methanol in air; this mixture is passed through the catalyst bed at a velocity of from 3,600 to 72,000, preferably from 24,000 to 36,000, litres, per litre of catalyst, per hour, expressed under normal temperature and pressure.

The following Examples illustrate the invention.

EXAMPLE 1

A gel containing iron and molybdenum in an atomic ratio of 2 is manufactured as follows:

202 g of ferric nitrate nonahydrate (0.5 gram-ion of Fe³⁺) and 176.6 g of ammonium paramolybdate tetrahydrate (1 gram-molecule of MoO₃) are crushed in a mortar. This results in a yellow powder which, when crushed in a mixer at room temperature, results in 15 minutes in a very viscous solution which transforms in 30 minutes, to a rubbery and transparent green gel containing 24% by weight of water.

EXAMPLE 2

The gel prepared in Example 1 is dehydrated for 2 days at 60°C in an oven to produce a transparent gel of brownish red colour, containing 2% by weight of water.

This gel is heated for 4 hours in an oven at 420°C in an air stream to produce a pro-

duct of intense green colour which has a specific surface area of 7.6 m²/g and an atomic ratio Mo/Fe of 2.

6 ml of this product is introduced into a vessel at 350°C. A gaseous mixture of air containing 6.6% by volume of methanol is then passed through the product at an hourly volumetric velocity of 24000 h⁻¹ for 6 hours. 99.8 molar % of the methanol is converted and the molar yield of formaldehyde is 96.9%.

EXAMPLE 3

176.6 g of ammonium paramolybdate tetrahydrate (1 mole MoO₃) is crushed in a mortar with 172.1 g of ferric nitrate nonahydrate (0.426 gram-ion of Fe³⁺) and 10 ml of water.

The resulting yellow paste is crushed for 30 minutes at room temperature and then for 30 minutes at 50°C in a mixer with sigmoid blades. The resulting transparent green gel is dehydrated at 70°C in an oven for 48 hours and then heated for 3 hours in a fixed bed at a temperature of from 400 to 450°C, under a light air stream to produce a green catalyst having a specific surface area of 4.4 m²·g⁻¹ and an atomic ratio Mo/Fe of 2.35.

EXAMPLE 4

6 ml of the catalyst prepared in Example 3 is placed in a reactor in the form of a bed and heated to about 350°C. Air containing 6.6% by volume of methanol is passed through the catalyst at an hourly volumetric velocity V.V.H. of 24000 h⁻¹ for 5 hours.

99.6 molar % of the methanol is converted and the molar yield of formaldehyde with respect to the methanol used is 94.6%.

EXAMPLE 5

The procedure of Example 3 is repeated, using manganese nitrate hexahydrate in place of a part of the ferric nitrate nonahydrate so as to obtain a catalyst having an atomic ratio Mo/(Fe+Mn) of 2.35 and an atomic ratio Mn/(Fe+Mn) of 0.08.

EXAMPLE 6

The procedure of Example 3 is repeated with a part of the ferric nitrate nonahydrate substituted by an equivalent amount of

chromium nitrate, and the addition of 100 g of ammonium nitrate to the mixture so as to obtain a catalyst having an atomic ratio Mo/(Fe+Cr) of 2.35 and an atomic ratio Cr/(Fe+Cr) of 0.08.

EXAMPLE 7

The procedure of Example 3 is repeated, except that a part of the ferric nitrate nonahydrate is substituted by an equivalent amount of cobalt nitrate hexahydrate, the ratio Mo/(Fe+Co) being 1.5.

EXAMPLE 8

The procedure of Example 3 is repeated except that a part of the ammonium paramolybdate is substituted by ammonium metatungstate containing 92.05% of tungstic anhydride. The ratio (Mo+W)/Fe is 2.

EXAMPLE 9

8.82 g of vanadyl oxalate, 88.3 g of ammonium paramolybdate tetrahydrate and 25 ml of an aqueous solution of hydrogen peroxide at 110 volumes are crushed in a mixer having sigmoid blades.

The resulting blue paste progressively becomes homogeneous and turn dark red in 30 minutes at 20°C.

A second mixture of 95.34 g of ferric nitrate nonahydrate (0.236 gram-ion of Fe³⁺) and 12.5 g of cobalt nitrate hexahydrate (0.042 gram-ion of CO²⁺) is manufactured separately and then added to the first mixture. The crushing is continued for 15 minutes at 20°C, and then for 1 hour at 45–50°C. The resulting product becomes homogeneous and hardens; it is then dehydrated at 65°C for 2 days, and heated for 3 hours at 420°C in an air stream to produce a catalyst having the following molar composition:

MoO ₃	:	72.46%
Fe ₂ O ₃	:	17.11%
V ₂ O ₅	:	4.20%
CoO	:	6.23%

The catalysts prepared in Examples 5 to 9 are tested under the conditions given in Example 2; the results are given in Table I below:

TABLE I

Example	M	N	Mo+N Fe+M	molar % conversion	molar % yield
100	5	Mn	2.35	99	95.4
	6	Cr	2.35	99.7	96.7
	7	Co	1.5	99.8	95.8
	8	W	2	99.6	95.7
105	9	V	..	97.2	95.1

WHAT WE CLAIM IS:—

1. A process for manufacturing a transparent gel containing molybdenum and iron, comprising mixing at least one molybdenum compound as hereinbefore defined with at least one ferric compound and, optionally, with at least one compound containing, in simple cationic form, a metal M selected from cobalt, nickel, manganese, chromium, scandium, yttrium, and the rare earth metals of atomic numbers from 57 to 71 inclusive, in the presence of a quantity of water not greater than that required to form individual saturated aqueous solutions of the compounds, and at a temperature between the freezing temperature of the saturated solutions of the compounds and 150°C, the compounds being used in such amounts that the atomic ratio $M/(Fe+M)$ is from 0 to 0.5 and the atomic ratio $Mo/(Fe+M)$ is from 0.4 to 5.
2. A process according to claim 1, in which ammonia is added to the molybdenum compound.
3. A process according to claim 1 or 2, in which an inorganic acid is added to the ferric compound.
4. A process according to claims 1, 2 or 3, in which ammonium chlorate ammonium perchlorate or ammonium nitrate is added to the reactants.
5. A process according to any preceding claim, in which the reactants are mixed by mechanical crushing.
6. A modification of a process according to any preceding claim, in which the molybdenum compound is also mixed with at least one compound containing, in the form of an oxygen-containing complex, a metal N selected from chromium, tungsten, manganese, vanadium and uranium, and the compounds are used in such amounts that each of the atomic ratios $M/(Fe+M)$ and $N(Mo+N)/(Fe+M)$ is from 0 to 0.5 and the atomic ratio $(Mo+N)/(Fe+M)$ is from 0.4 to 5.
7. A process according to claim 6, in which the molybdenum compound is ammonium molybdate, the ferric compound is ferric nitrate and the atomic ratio $(Mo+N)/(Fe+M)$ is from 1.5 to 5.
8. A process according to any preceding claim, in which the product is dried at a temperature of from 40 to 150°C.
9. A process according to claim 1, substantially as hereinbefore described in any one of Examples 1, 3, 5, 6 and 7.
10. A process according to claim 7, substantially as hereinbefore described in Example 8 or 9.
11. A process according to any one of claims 1—7, in which the product is mechanically crushed at a temperature of from 20 to 150°C for at least 2 hours to produce a powdered substance having a water content of lower than 10% by weight.
12. A process according to claim 11, in which the powdered substance is dried at a temperature of from 40 to 150°C.
13. A gel, when obtained by a process according to any one of claims 1—10.
14. The use of a gel according to claim 13 as a light filter.
15. A powdered substance, when obtained by a process according to claim 11 or 12.
16. The process that comprises heating a gel according to claim 13 or a powdered substance according to claim 15 at a temperature of from 300 to 500°C to produce a mixed oxide.
17. The process that comprises heating a gel according to claim 13 or a powdered substance according to claim 15, in which the atomic ratio $Mo/(Fe+M)$ or $(Mo+N)/(Fe+M)$ is from 1.5 to 5, at a temperature of from 300 to 500°C to produce a catalyst.
18. A process according to claim 16 or 17, in which the gel is shaped by extruding, pilling, crushing or pouring and fragmenting before drying and heating.
19. A process according to claim 16 or 17, in which the powdered substance is used and is shaped by pilling, extruding or granulating before heating.
20. A process according to claim 17, substantially as hereinbefore described in any one of Examples 2, 3 and 5—9.
21. Mixed oxides, when obtained by a process according to claim 16, 18 or 19.
22. Catalysts, when obtained by a process according to claim 17, 18 or 19.
23. Catalysts according to claim 22, further comprising a catalytically inert material.
24. The process that comprises oxidizing an alcohol to an aldehyde in the presence of a catalyst according to claim 22 or 23.
25. A process according to claim 24, in which the alcohol is methanol and the aldehyde is formaldehyde.
26. A process according to claim 24, substantially as hereinbefore described in any one of Examples 2, 4 and 9.
27. Aldehydes, when obtained by a process according to claim 24, 25 or 26.

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